COMPOSITIONAL VARIABILITY AMONG 74220 ORANGE GLASS BEADS AND THEIR CRYSTALLIZED EQUIVALENTS.

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Inspired by John Delano's recent work [1] that showed small but systematic differences in the compositions of individual 74220 orange glass beads, we have begun a high-precision instrumental neutron activation analysis (INAA) study of the trace element compositions of orange glass beads and their black crystallized equivalents. The major element compositional differences among glass beads amount to only a few percent relative [1], therefore, highly-precise electron microprobe (EMP) techniques must be employed to discern these chemical variations. If trace-element compositional variations are on the same scale, any potential analytical technique must have a precision of much less than 1% (relative) to resolve these differences. Clearly, secondary ion mass spectrometry (SIMS) techniques with precisions of ~12% [2] are woefully inadequate for this work. INAA, on the other hand, provides precisions of <2% relative for some minor and trace elements [3], much closer to the required precision.

This preliminary study of ten orange glass beads was undertaken to evaluate whether the precision of micro-INAA [4] could be improved to find these small compositional differences. Ten glassy beads and 27 crystallized beads ~200-300 μm in diameter were hand-picked from 74220,121, washed in acetone, and cleaned in distilled water in an ultrasonic bath for ~20 minutes to remove adhering materials. Samples were irradiated for 25 hours in a flux of 3×10^{14} cm^{-2}sec^{-1} at Brookhaven National Laboratory and at least three gamma-ray spectra were obtained on each sample using large intrinsic Ge detectors. Sample spectra from 24 hour "long counts" typically contained 3×10^7 counts.

INAA results from ten gamma-ray spectra of a single particle had relative standard deviations <0.2% for the most favorable elements (Sc, Cr, Fe, Co). Individual 74220 beads weigh ~10-30 μg, too small to weigh to high accuracy (microbalance uncertainties are $\pm$0.5-1.0 μg, or ~3-10% relative). As will be discussed below, FeO did not vary among beads within our ability to measure it with EMP or INAA. We therefore corrected the measurement uncertainties by normalizing to 23.1 wt. % FeO.

After INAA, the beads were analyzed using high-precision techniques modified from [5] on the Cameca SX-100 EMP located at JSC. Microprobe beam current and counting times were chosen so that at least 10^6 X-ray counts were obtained for each element. The spectrometers were kept fixed during the analyses to eliminate uncertainty due to mechanical imprecision in the spectrometer mechanisms. Analyses were performed in two steps, with five elements analyzed together in each step. The uncertainty due to counting statistics is approximately 0.1%, and observed standard deviations of multiple analyses on single beads were comparable (~0.1-0.2%). Count rates were normalized to Faraday cup current and compared to a standard orange glass bead. The resulting abundances were adjusted to give averages in agreement with [1]. We stress that, for

the purposes of this study, we are primarily interested in bead-to-bead variations, not the actual values, and we acknowledge that these data may be slightly inaccurate due to our normalization and adjustment procedure.

Compositional variations

Our EMP major element analyses span the range of the 'high-Si' and 'low-Si' groups of [1] but we analyzed too few spherules to confidently distinguish between the two groups. We observe the same inverse correlation between MgO and CaO abundances described by [1] (Fig. 1a), as well as inverse correlations between MgO and Al$_2$O$_3$, and MgO and TiO$_2$.
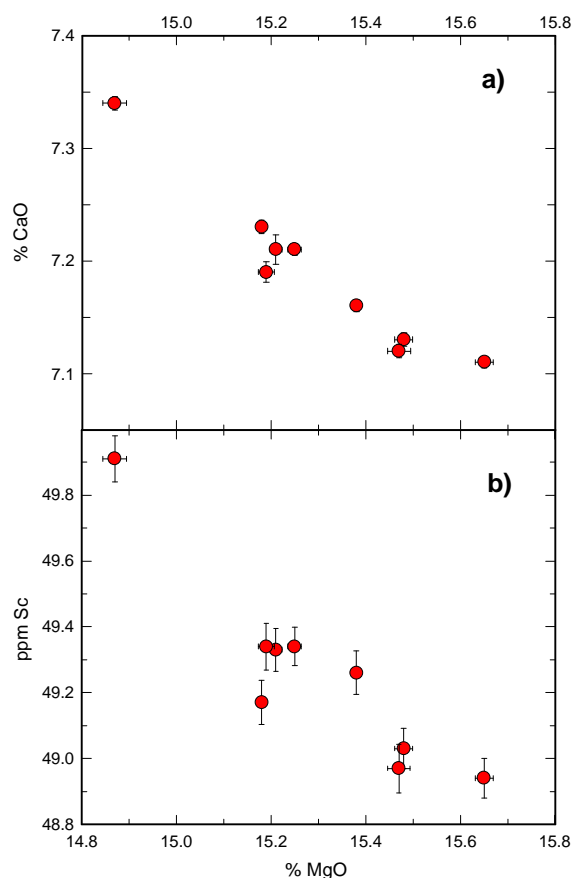

Fig. 1 Analyses of 74220 orange glasses. Error bars are standard deviations of ~6 analyses of each bead in a), and estimated one sigma uncertainties (primarily counting statistics) in b).

Sc and Sm abundances (determined by INAA) also display inverse correlations with MgO (Fig. 2). Co and Cr, on the other hand, do not vary systematically with MgO. It appears that those elements that are incompatible in olivine inversely correlate with MgO, and elements that are compatible to mildly incompatible in olivine do not. K and Na vary by as much as 10% (relative) among our 10 spheres. Delano et al. [6] observed Na-diffusion profiles in some spheres indicating diffusive gain of Na. Using the EMP, we

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also observed these diffusion patterns in some beads, as well as systematic variation between Na and K abundances, but there are no systematic relationships between the alkalis and any other element in our INAA data set.
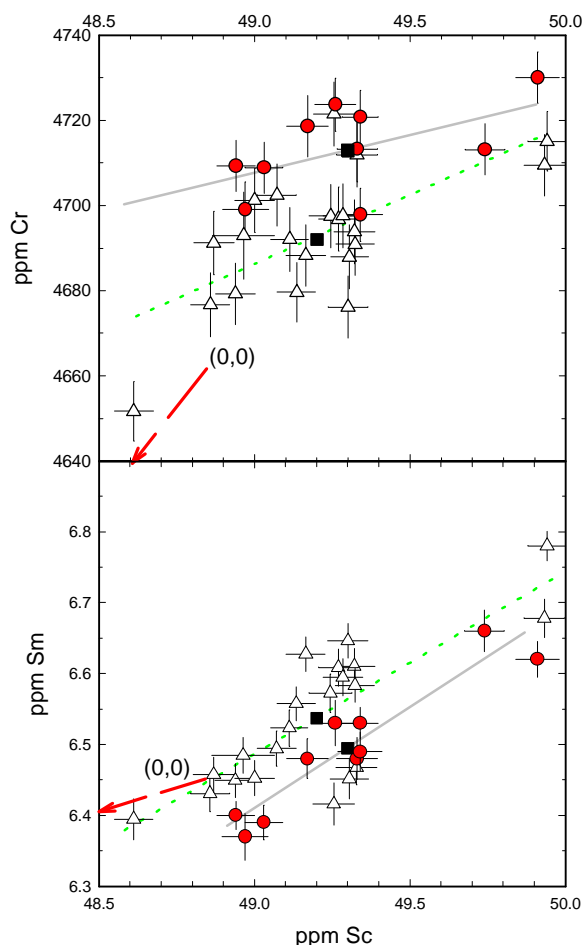

Fig. 2 INAA analyses of 74220 orange glasses (filled circles) and crystallized "black beads" (open triangles). Error bars are estimated 1σ uncertainties. Solid squares represent the averages of each group, and the solid and dotted lines are regressions through each group's data. Heavy arrows point toward the origins, showing that the observed trends are not artifacts of the normalization.

The 74220 magma underwent no discernible pre-eruptive crystal fractionation [e.g., 3,7], so the observed chemical trends must reflect dynamic magmatic processes that occurred within the lunar mantle source, such as mixing of melt derived from different regions of a chemically-heterogeneous mantle, or incomplete mixing of compositionally-different melts during the ascent of a lunar mantle diapir [1,8]. It is hoped that high-precision trace-element data will lead to better models for these processes.

INAA analyses of crystalline beads

To our knowledge, whole individual crystallized spherules have never been analyzed, primarily because their microcrystalline texture makes microbeam analyses difficult. Previous data on the crystallized glasses suggest that they have approximately the same bulk composition as their non-crystalline counterparts, but high-precision analyses do not exist. INAA is free of matrix and spatial effects and is equally well-suited for the analysis of crystalline and homogeneous samples. Again, the point of this study is to identify compositional variations among 74220 glasses so that we might gain some insight into lunar mantle processes. So far, only very limited variations (<8% relative, except for the alkalis) have been observed, and it is difficult to rigorously model such small compositional trends. Crystallized "black beads" are important components of the 74220 soil and might conceal even more compositionally-diverse material, so we performed INAA on a set of 27 crystallized beads to search for further compositional heterogeneity in the 74220 eruptives.

The masses of the crystallized spheres range from 15-38 μg, slightly larger than the glasses (11-26 μg). The average FeO concentration of the 27 black beads is identical to the average orange glass bead, so the analyses of individual black beads were normalized to FeO=23.1%. Six of the beads were enriched in Co (by up to 10%) and Ni, apparently because they contain anomalous concentrations of exsolved metal [8], and were removed from the dataset.

Although the compositions of the crystallized and glassy beads are very similar, there appear to be real differences between crystalline and glassy beads. The crystalline beads are distinctly lower in Cr and higher in Sm (Fig 2a,b), although there is some overlap between the two data sets, and the crystalline beads seem to fall on distinct trends when plotted against Sc, much like the trends vs. MgO shown in Fig. 1. Clearly, more data are needed to confirm the compositional differences, but if the differences are real, they raise interesting questions regarding the nature of the lunar eruptions. For example, do the crystallized and glassy beads represent liquid droplets erupted at different times during the event? In this model, the crystallized beads may have been suspended for a longer period of time in the optically-dense portion of the fire fountain so that they cooled relatively slowly and crystallized [9]. Later, these crystallized spheres could have been co-deposited with glassy beads that were erupted in a cooler portion of the fire fountain. This model implies that the composition of the erupted material changed with time. An alternative is that the cystallized and glassy beads were erupted simultaneously from different parts of a fissure-type eruption, with the composition of the magma slightly different at different locations in the vent.

Of course, these models are speculative, but they serve to illustrate the nature of the constraints that may be provided by further study of the 74220-type orange glasses and their crystalline equivalents.

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